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(54) PRODUCTION OF BISPHENOL A

(57)Abstract:

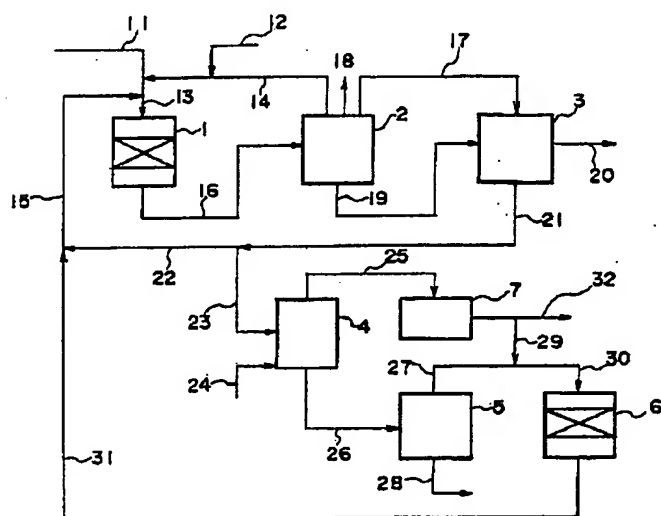
PROBLEM TO BE SOLVED: To provide a method for producing bisphenol A in high yield by limiting the amount of water in a recombination step, comprising a formation step for forming the bisphenol A by carrying out condensation reaction of acetone with phenol in the presence of a specific catalyst, a crystallization step for cooling the product, a degradation step for degrading a mother liquor and the recombination step.

SOLUTION: This method for producing bisphenol A in high yield comprises limiting of the amount of water to ≤ 0.1 wt.% in a recombination step after forming the bisphenol A by carrying out a condensation reaction of acetone with phenol in the presence of a strong acid ion exchange resin partially modified by a sulfur-containing amine compound (e.g. 2-mercaptoethylamine).

[Claim(s)]

[Claim 1] The manufacture method of bisphenol A which is equipped with the following and characterized by controlling the moisture content in the reaction generation liquid in this recombination process to 0.1 or

less % of the weight. (i) The bisphenol A generation process to which the condensation reaction of an acetone and the phenol of an excessive amount is carried out under existence of the strong acid nature ion-exchange-resin catalyst which denaturalized partially with the ** sulfur amine compound. (ii) Crystallization process which the resultant which consists of bisphenol A obtained at this bisphenol A generation process and a phenol is cooled [process], and makes bisphenol A / phenol crystal adduct, and a mother liquor generate. (iii) The decomposition process which heat-treats the obtained mother liquor under existence of an alkaline catalyst, and decomposes bisphenol A in a mother liquor, and its isomer into a phenol and an isopropenyl phenol. (iv) The recombination process which contacts the decomposition generation liquid obtained at this decomposition process for a strong acid nature ion-exchange-resin catalyst, makes the phenol and isopropenyl phenol which are contained in this decomposition generation liquid recombine, and makes bisphenol A generate, and ** which makes the bisphenol A generation process circulate through the recombination generation liquid (v) Obtained.



drawing 1

DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[The technical field to which invention belongs] this invention relates to the manufacture method of bisphenol A.

[0002]

[Description of the Prior Art] Making an acetone and a superfluous phenol react under existence of an acid catalyst, and manufacturing bisphenol A is known. In this method, although bisphenol A is obtained as a phenol solution, it is sent to a crystallization process, and is cooled here, and this thing is separated as a bisphenol / a phenol crystal adduct, after removing the low boiling point fraction and the superfluous phenol which carry out distillation processing and are contained in it. Although the phenol solution containing by-products, such as bisphenol A and its isomer, and the coloring impurity of **** small quantity is obtained as a mother liquor in a crystallization process, when circulation reuse of this mother liquor is carried out as it is at the bisphenol A generation process, since accumulation of the aforementioned by-product or a coloring impurity takes place, it is on the other hand, necessary to perform removal of those by-products and impurities. For this reason, after shunting a part of mother liquor [at least] toward the bisphenol A generation process on the occasion of circulation reuse, heating a mother liquor under existence of an alkaline catalyst and decomposing into a phenol and an isopropenyl phenol, make these compounds react in a recombination process, it is made to change into bisphenol A, and this bisphenol A is circulated for the phenol and the acetone to the bisphenol A generation process which carries out a condensation reaction. By the way, in the aforementioned decomposition process, if it circulates through the reaction generation liquid from a recombination process to the condensation-reaction

process of an acetone and a phenol in order to carry out the byproduction of the matter used as a catalyst poison component to the catalyst used at the condensation-reaction process of an acetone and a phenol, the catalyst of the condensation-reaction process will receive poisoning, and will produce the problem that the activity falls. Although it is necessary to exchange for a new catalyst the catalyst which carried out the activity fall, when requiring much time and effort, it is remarkably [economically or] disadvantageous for such catalyst exchange.

[0003]

[Problem(s) to be Solved by the Invention] After this invention decomposes the mother liquor obtained at bisphenol A / phenol crystal adduct crystallization process under an alkaline catalyst, Contact the obtained decomposition generation liquid for a strong acid nature ion-exchange-resin catalyst, and the phenol and isopropenyl phenol which are contained in decomposition generation liquid are made to recombine with bisphenol A. Let it be the technical problem to offer the method of suppressing effectively activity degradation of the catalyst in the condensation-reaction process in the method of circulating the obtained recombination-reaction generation liquid to the condensation-reaction process of an acetone and a phenol.

[0004]

[Means for Solving the Problem] As a result of repeating research wholeheartedly that the aforementioned technical problem should be solved, by controlling the moisture in reaction generation liquid [in / a recombination process / unexpectedly] to 0.1 or less % of the weight, this invention persons find out that the aforementioned technical problem can be solved, and came to complete this invention. Namely, the bisphenol A generation process to which the condensation reaction of an acetone and the phenol of an excessive amount is carried out under existence of the strong acid nature ion-exchange-resin catalyst which denaturalized partially with (i) ** sulfur amine compound according to this invention, (ii) The resultant which consists of bisphenol A obtained at this bisphenol A generation process and a phenol is cooled. Bisphenol A / phenol crystal adduct, and the crystallization process that makes a mother liquor generate, The obtained mother liquor is heat-treated under existence of an alkaline catalyst. (iii) The decomposition process which decomposes bisphenol A in a mother liquor, and its isomer into a phenol and an isopropenyl phenol, (iv) The recombination process which contacts the decomposition generation liquid obtained at this decomposition process for a strong acid nature ion-exchange-resin catalyst, makes the phenol and isopropenyl phenol which are contained in this decomposition generation liquid recombine, and makes bisphenol A generate, (v) It consists of making the bisphenol A generation process circulate through the obtained recombination generation liquid, and the manufacture method of bisphenol A characterized by controlling the moisture content in the reaction generation liquid in this recombination process to 0.1 or less % of the weight is offered.

[0005]

[Embodiments of the Invention] Next, this invention is explained, referring to a drawing. Drawing 1 shows one example of the flow sheet in the case of enforcing the method of this invention. this drawing -- setting - 1 -- in a crystallizer and 4, a distilling column and 5 show a cracking unit (purge equipment), and 6 shows [the condensation reactor of an acetone and a phenol, and 2 / a distilling column and 3] recombination equipment (scavenger equipment) In order to enforce the method of this invention according to drawing 1 , while supplying a raw material phenol through a line 11 to the condensation reactor 1, a raw material acetone is supplied through a line 12, a circulation acetone is supplied through a line 14, and circulation bisphenol A is further supplied through a line 15. The catalyst which consists of strong acid nature ion exchange resin which denaturalized partially is filled up into the condensation reactor 1 with the ** sulfur amine compound. As strong acid nature ion exchange resin in this case, a sulfonic-acid type cation exchange resin can be used. Although such a sulfonic-acid type cation exchange resin is known well conventionally and the thing of a gel type or a porous type can be used for it, a desirable gel type thing is used. As for the degree of cross linking, it is preferably good to specify in 2 - 6% of range 2 to 16%. Moreover, the mean particle diameter is usually 0.4-1.5mm preferably 0.2-2mm. The sulfonic-acid type cation exchange resin of such native is already marketed, for example, can use preferably loam and the Amberlite made from HASU, Amberlyst, DAYAION by Mitsubishi Kasei Corp., etc.

[0006] Although the aforementioned sulfonic-acid type cation exchange resin denaturalizes the part with a ** sulfur amine compound and it is used for it as a catalyst With the compound with which the ** sulfur amine compound in this case was also known well conventionally For example, 3-mercapto methylpyridine, 3-mercapto ethyl pyridine, Mercapto alkyl pyridines, such as 4-mercapto ethyl pyridine; 2-mercapto ethylamine, Mercapto alkylamines, such as 3-mercapto butylamine and a 3-n-propylamino-1-propyl mercaptan (or amino alkyl mercaptan); Thiazolidine, Thiazolidine, such as 2 and 2-dimethyl

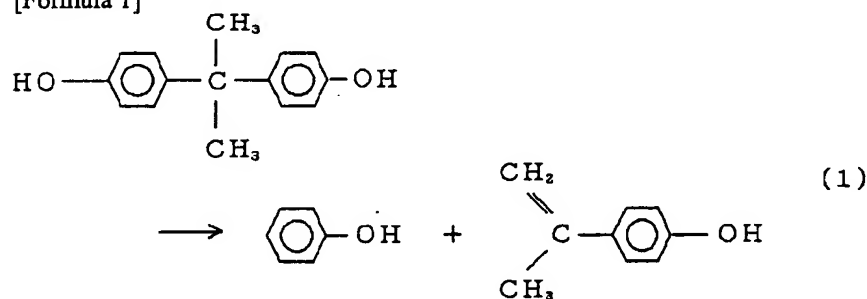
thiazolidine, cycloalkyl thiazolidine, 2-methyl-2-phenyl thiazolidine, and 3-methyl thiazolidine; amino thiophenols, such as a 1 and 4-amino thiophenol, etc. are mentioned. It is 2-mercapto ethylamine and 2, and 2-dimethyl thiazolidine especially preferably. Said ** sulfur amine compounds can be the addition salts and quaternary ammonium salt of the acid matter, such as a hydrochloric acid.

[0007] In the condensation reactor 1, the condensation reaction of an acetone and a phenol occurs and bisphenol A is generated. reaction temperature -- the temperature beyond the melting point of a phenol -- 40-100 degrees C is usually 55-85 degrees C preferably Reaction pressure is an ordinary pressure or fine pressurization preferably one to 1.5 atmospheric pressure. Reaction time is 50 - 120 minutes preferably for 15 to 200 minutes. The 8-20 mols of the amount of the phenol used are 10-16 mols preferably to one mol of acetones. It is sent to a distilling column 2 through a line 16, distillation processing is carried out here, and the reaction generation liquid obtained with the condensation reactor 1 is divided into the phenol solution containing an acetone, water, a phenol, and bisphenol A. An acetone passes along a line 14, and circulates through it to the condensation reactor 1, and water is discharged out of a system through a line 18. A phenol is introduced as a phenol for washing through a line 17 to a crystallizer 3.

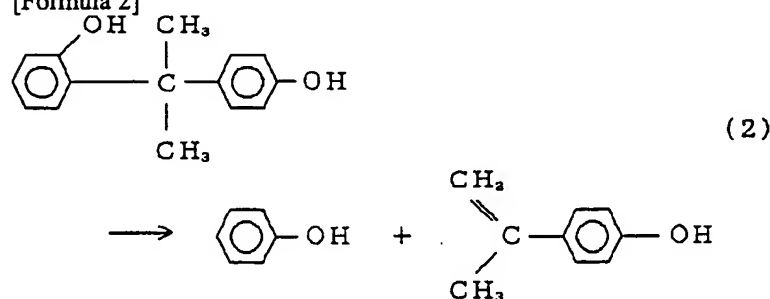
[0008] The phenol solution containing bisphenol A from which the low boiling point fraction was separated in the distilling column 2 is sent to a crystallizer 3 through a line 19, and is cooled here. Thereby, bisphenol A / phenol crystal adduct, and a mother liquor are generated. Bisphenol A / phenol crystal adducts are collected through a line 20, after a solid-liquid separation method dissociates from a mother liquor and being washed by the washing phenol. The mother liquor obtained by the crystallizer 3 consists of a phenol solution containing bisphenol A and its by-product, and the bisphenol A isomers, such as 2 and 4'-bisphenol A, a tris phenol, a little coloring impurity, etc. are included as a by-product. This mother liquor is sent to a distilling column 4 through a line 21 and a line 23, distillation processing is carried out here, the phenol fraction contained in a mother liquor is separated as a low boiling point fraction, and this thing is introduced into a condenser 7 and condensed.

[0009] The solution of the alkaline matter is introduced near the bottom of a distilling column 4 through a line 24. In the alkaline solution introduced in the distilling column, the moisture is distilled from the overhead and, on the other hand, the alkaline matter is sent to a cracking unit 5 through a line 26 with the bottom fraction (bisphenol A fraction) of a distilling column 4. A cracking unit 5 is equipment which has the structure like a reaction distillation apparatus. The bottom fraction of the distilling column 4 introduced into the cracking unit 5 is heated under coexistence of the alkaline matter here. Bisphenol A contained in a bottom fraction and its isomer are decomposed into a phenol and an isopropenyl phenol by this heating. The reaction in this case is expressed with the following formula.

[Formula 1]



[Formula 2]



The aforementioned reaction formula (1) shows the decomposition reaction of bisphenol A, and the

aforementioned reaction formula (2) shows the decomposition reaction of the bisphenol A isomer. Each of bisphenol A and its isomer is decomposed into a phenol and an isopropenyl phenol.

[0010] As the aforementioned alkaline matter, the hydroxide of alkaline earth metal, such as the hydroxide of alkali metal, such as sodium and a potassium, an oxide, a carbonate, various phenol salts, calcium, and magnesium, an oxide, a carbonate, various phenol salts, etc. are mentioned. These alkaline matter is preferably introduced near the pars basilaris ossis occipitalis of a distilling column 4 as 0.01 - 0.5% of the weight of solution 0.005 - 0.8 % of the weight of concentration. 200-350 degrees C of reaction temperature in a cracking unit 5 are 200-300 degrees C preferably. reaction pressure -- 5 torrs - an ordinary pressure -- it is 10-150 torrs preferably In a cracking unit 5, although decomposition of bisphenol A and its isomer takes place as mentioned above, a high boiling point tarry material carries out a byproduction simultaneously. This tarry material is discharged out of a system through a line 28 from the pars basilaris ossis occipitalis of a cracking unit 5. The decomposition generation liquid which consists of a phenol obtained in a cracking unit 5 and an isopropenyl phenol is introduced into recombination equipment 6 through lines 27 and 30. Moreover, the condensate which contains in this recombination equipment the phenol condensed with the condenser 7 is supplied through a line 29.

[0011] Recombination equipment 6 is filled up with the strong acid nature ion-exchange-resin catalyst, and the isopropenyl phenol of the phenol introduced into recombination equipment 6 contacts this catalyst, starts a condensation reaction, and is changed into bisphenol A. It circulates through the reaction generation liquid obtained with recombination equipment 6 to the condensation reactor 1 through lines 31 and 15. As a catalyst with which recombination equipment 6 is filled up, strong acid nature ion exchange resin is used. With a ** sulfur amine compound, this resin is denaturalized partially and can also be used. 45-120 degrees C of reaction temperature of recombination equipment 6 are 50-85 degrees C preferably. Reaction pressure is an ordinary pressure or fine pressurization preferably one to 1.5 atmospheric pressure. Reaction time is 15 - 120 minutes preferably for 5 to 200 minutes.

[0012] In this invention, the moisture in the reaction generation liquid in recombination equipment 6 is preferably held to 0.06 or less % of the weight 0.1 or less % of the weight. The bird clapper was found out that the catalyst poison component which exists in supply liquid tends to stick to the resin, so that the moisture concentration in the supply liquid became low, when the supply liquid which contains in the strong acid nature ion-exchange-resin catalyst in recombination equipment 6 the decomposition generation liquid obtained by the cracking unit 5 was contacted according to research of this invention persons. this invention reduces the amount of the catalyst poison component accompanied into bisphenol A through which it circulates from recombination equipment to the condensation reactor 1, prevents the catalyst poisoning in the condensation reactor 1, and makes the catalytic activity stabilized over the long time hold by making a catalyst poison component stick to the strong acid nature ion-exchange-resin catalyst in recombination equipment, and removing it. It is not desirable to produce degradation in activation of the catalyst which the condensation reactor 1 becomes with far big equipment compared with recombination equipment 6, and can set this condensation reactor 1. In the case of this invention, recombination equipment 6 shows the operation as a guard reactor to the condensation reactor 1.

[0013] As the moisture in the reaction generation liquid of recombination equipment 6 is shown in drawing 1 as a method for making it decrease to 0.1 or less % of the weight, while arranging a distilling column 4 in the upstream of a cracking unit 5, a mother liquor can be distilled in a distilling column 4, and how to introduce into a cracking unit 5 only the bottom fraction by which bisphenol A and its isomer were condensed can be shown. Since only the bottom fraction of a distilling column 4 is introduced into a cracking unit 5, and the amount of the processed raw material introduced into a cracking unit 5 is streamlined when carrying out decomposition processing, the amount of supply of the solution of the alkaline matter and the amount of water which is little, and ends, consequently is introduced into recombination equipment 6 are streamlined inevitably.

[0014] Among the solution of the alkaline matter introduced into the distilling column 4, moisture is distilled as a **** fraction of a distilling column 4, and is condensed in a condenser 7. therefore, a part of condensate of a condensate 7 -- base -- the moisture content introduced into recombination equipment 6 can be decreased by dissociating outside

[0015]

[Example] Next, an example explains this invention to a detail further.

[0016] Bisphenol A was manufactured according to the flow sheet shown in example 1 drawing 1 . The main operating conditions in that case are shown below.

(1) condensation reactor 1 (i) reaction concentration: -- 70 degrees C (ii) a phenol / acetone mole-ratio: --

13 (iii) catalyst: -- 10% of the sulfonic group of a sulfonic-acid type cation exchange resin by 2-mercapto ethylamine Thing (2) distilling column 2 which denaturalized (i) The **** fraction composition acetone which passes along a line 14 : [97.6wt% water] : 1.0wt% others : 1.4wt% (ii) The overhead fraction composition phenol which passes along a line 17: 99.5wt% others : 0.5wt% (iii) Drainage water which passes along a line 18 : 99.95wt% phenol : 0.05wt% (iv) Bottom fraction composition bisphenol A which passes along a line 19: 22wt% phenol A : 74wt% others : 4wt% (3) crystallizer 3 (i) Mother liquor composition bisphenol A : 7.7wt% bisphenol A isomer: 2.4wt% phenol : 86.3wt% others : 3.6wt% [0017] (4) Distilling column (i) **** fraction composition phenol : 99.8wt% water : 0.05wt% others : 0.15wt% (ii) Bottom fraction composition bisphenol A : 48.5wt% bisphenol isomer: 14.8wt% phenol : 14.8wt% alkalinity matter : 0.05wt% (NaOH) in addition -- :21.85wt% (iii) -- alkaline catalyst (line 24) 25wt% solution (5) cracking unit 5 of NaOH (i) Reaction temperature: 250 degrees C (ii) Pressure : 40-torr (iii) decomposition-product composition (line 27) Phenol :54wt% isopropenyl phenol: 28wt% others : 18wt%(6) recombination equipment 6 (i) Reaction temperature: 55 degrees C (ii) Catalyst: Sulfonic-acid type cation-exchange-resin (iii) feed-stock composition (line 30) Phenol :92.6wt% isopropenyl phenol: 4.4wt% moisture : 0.04wt% others : 2.96wt% (iv) Reaction generation liquid composition phenol : 89.5wt% bisphenol A: 8.0wt% moisture : 0.04wt% others : 2.46wt% [0018] When the manufacture experiment of bisphenol A was conducted on the aforementioned conditions according to the flow sheet of drawing 1 , using a phenol and an acetone as a raw material, the acetone invert ratio [reaction start 2000 hour] only fell to only 90% from 92% of acetone invert ratios in early stages of a reaction. [0019] It experimented like the example 1 using the 2wt% solution of NaOH supplied to example of comparison 1 distilling column 4 except having made the moisture concentration in the supply liquid (line 30) to recombination equipment 6 increase to 0.5wt(s)%. Consequently, the acetone invert ratio [reaction start 2000 hour] fell sharply with 85% from 92% of acetone invert ratios in early stages of a reaction. [0020] [Effect of the Invention] According to this invention, activity degradation of the catalyst in the ligation reaction equipment of the acetone and phenol which constitute main reactors in manufacture of bisphenol A can be suppressed effectively, and reduction-ization of the manufacturing cost of bisphenol A can be attained.